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Surface π bonding and the near-first-order desorption kinetics of hydrogen from
Ge(100)2 \times 1

by

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Surface π bonding and the near-first-order desorption kinetics of hydrogen from Ge(100)2 \times 1

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Abstract

We show by temperature-programmed desorption that hydrogen desorbs from Ge(100)2 \times 1 near 570 K with near-first-order kinetics, similar to the behavior of hydrogen on Si(100)2 \times 1. The near-first-order desorption kinetics are attributed to pairing on surface dimers induced by the π bond on unoccupied dimer atoms, and a pairing enthalpy of 5 \pm 1 kcal/mol is inferred. However, a comparison between the pairing enthalpies for H atoms on Ge(100) and Si(100) with the electronic structure of the respective *clean* surfaces indicates that estimates of the π bond strength based on the surface band structure do not correlate with the propensity for pairing.

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The kinetics and dynamics of hydrogen desorption from Si(100)2×1 have been a major focus of recent effort. Hydrogen chemisorption has proved a useful complement to studies of geometric and electronic structure of semiconductor surfaces and plays a critical role in the growth of Si and Ge_xSi_{1-x} thin films by chemical vapor deposition and atomic layer epitaxy. Much of the recent work was stimulated by the discovery that recombinative hydrogen desorption follows first-order kinetics on Si(100),^{1,2} in contrast to the second-order behavior seen on metal surfaces. The original proposal by Sinniah *et al.*¹ that the first-order kinetics results from the rate-limiting excitation of hydrogen atoms to a band-like delocalized state was contradicted by observations of near-second-order desorption kinetics of hydrogen from Si(111),²⁻⁴ by measurements of the diffusion kinetics of hydrogen on Si(111) which suggest conventional hopping,⁵ and by dynamical measurements showing that desorbing H₂ is rotationally cold and vibrationally hot, implying a highly symmetric transition state.⁶ Wise *et al.*² suggested that the first-order desorption kinetics are due instead to pairing of hydrogen on the dimerized surface atoms, and Boland⁷ and we⁸ proposed that preferential pairing of H atoms is a consequence of the π bond^{9,10} on "unoccupied" dimers. Boland obtained direct evidence for preferential pairing by scanning tunneling microscopy (STM) and estimated a π bond strength of ≈ 18 kcal/mol from tunneling spectra above un- and singly-occupied dimers.⁷ We reviewed existing evidence for π bonding and preferential pairing and proposed a doubly-occupied dimer model to quantitatively describe the desorption kinetics.⁸ The driving force for pairing, ΔH_{pair} , is equal to the difference in Si-H bond strengths between doubly-occupied dimers, with two hydrogen atoms, and singly-occupied dimers, with one hydrogen atom, and was identified with the π bond strength⁸ by analogy to molecular π bonds.¹¹ ΔH_{pair} was estimated as ≈ 7.5 kcal/mol by comparing model predictions to temperature-programmed desorption (TPD) data^{1,2} indicating slight departures from first-order kinetics.⁹ Höfer *et al.* demonstrated that the kinetics do indeed deviate from first-order at low coverage, and used our model to obtain a refined determination of 6 ± 1 kcal/mol for ΔH_{pair} .¹² A modest value for ΔH_{pair} is supported by high-level *ab initio* calculations of Si-H bond strengths in a cluster analogue of Si(100)2×1 that imply values of 2-5 kcal/mol.^{13,14}

The interaction of hydrogen with Ge(100)2×1, which has received much less attention, provides a test for the predicted generality of preferential pairing^{7,8} and also offers insight into the relationship between ΔH_{pair} , the π bond strength, and the surface electronic structure. The behavior of hydrogen on germanium is qualitatively very similar to that on silicon. At coverages up to one monolayer a (2×1):H monohydride structure is formed;¹⁵⁻¹⁷ a less-stable dihydride can be formed at higher coverages.¹⁷ H₂ desorbs from Ge(111) with near-second-order kinetics,¹⁸ just as on Si(111).²⁻⁴ Adsorption of hydrogen on Ge(100) was investigated in early work¹⁸ but TPD results were not reported. We found that H₂ resulting from decomposition of H₂S or H₂O on Ge(100) desorbs with approximately first-order kinetics near 570 K, implying an activation energy for desorption near 40 kcal/mol.¹⁹ The rate-limiting step in [100] growth of germanium from Ge₂H₆, presumably H₂ desorption from Ge(100)2×1, was found by reflectometry to follow first-order kinetics with an activation energy of 40 kcal/mol.²⁰ In the present work we demonstrate that the

desorption kinetics of H_2 from $Ge(100)2\times 1$ show systematic deviations from first-order behavior in the low coverage limit which can be quantitatively described by the doubly-occupied dimer model. Comparison of the inferred value of ΔH_{pair} with the surface electronic structure of $Ge(100)$ shows that estimates of the π bond strength based on the band structure of clean $Ge(100)$ and $Si(100)$ do not correlate with the propensity for pairing of H atoms. However, experiments on *nearly-hydrogen-saturated* surfaces might allow for a spectroscopic determination of the π bond strength.

Experiments were performed in an ultrahigh vacuum (UHV) chamber equipped with LEFD/ESDIAD optics, an Auger spectrometer, a quadrupole mass spectrometer (QMS) with a water-cooled shroud, an ion gun, and a tungsten filament for dosing of atomic hydrogen.¹⁹ The $Ge(100)$ sample was cleaved from a 0.25-mm-thick n-type wafer, $\rho = 5\text{--}40\ \Omega\ \text{cm}$, to a dimension of $13.4\ \text{mm} \times 13.8\ \text{mm}$. A chromel-alumel thermocouple was cemented into a small hole drilled near one edge. After degreasing, the Ge sample was placed in the chamber and cleaned by several sputter-and-anneal cycles ($i_{\text{Ar}^+} = 2\text{--}4\ \mu\text{A}\ \text{cm}^{-2}$, $E_{\text{Ar}^+} = 500\ \text{V}$, $T_{\text{anneal}} = 850\ \text{K}$).

Atomic hydrogen exposures were performed by backfilling the UHV chamber with H_2 to pressures of $2\times 10^{-8}\text{--}5\times 10^{-7}$ Torr and heating a coiled W filament located $\approx 3\ \text{cm}$ from the sample to 1700–1800 K. After dosing, when the background pressure fell to $2\text{--}3 \times 10^{-10}$ Torr, the sample was rotated to face the entrance slit of the QMS shroud, at a distance of $\approx 0.5\ \text{cm}$. The temperature was ramped at $2\ \text{K}\ \text{s}^{-1}$ and the QMS signal for $m/e=2$ was recorded by an AT-compatible personal computer. A coverage calibration for hydrogen was obtained by TPD of H_2S , whose adsorption as $H + SH^{21}$ saturates at 0.5 monolayer,²² and which yields exclusively H_2 and GeS upon heating.¹⁹

TPD traces for H_2 following atomic hydrogen exposures are shown in Fig. 1 for various initial coverages, Θ_0 . The peak desorption temperature, T_p , at all initial coverages is about 570 K. The nearly coverage-independent values of T_p , together with the asymmetric peak shape at high Θ_0 , indicate near-first-order desorption kinetics.²³ However, the slight but readily discernable increase in T_p and the more symmetric peak shape at lower Θ_0 demonstrate a departure from first-order kinetics.⁸ The dependence of T_p on Θ_0 is shown in Fig. 2 together with model predictions.

The doubly-occupied dimer model comprises an exact solution to a lattice gas model which incorporates preferential pairing of adsorbates on dimers but neglects interactions between dimers.⁸ The coverage of hydrogen which is paired on surface dimers is given by^{8,24}

$$\Theta_2 = \Theta - \frac{2\Theta(1-\Theta)}{\{1 + 4[\exp(\Delta H_{\text{pair}}/RT) - 1]\Theta(1-\Theta)\}^{1/2} + 1} \quad (1)$$

where Θ is the instantaneous total coverage of hydrogen, R is the gas constant, and T is the temperature. The assumption of quasiequilibrium, i.e., that hydrogen diffusion is fast compared to desorption, is supported by measurements of diffusion and desorption kinetics of hydrogen on $Si(111)^{4,5}$ and $Si(100)$.¹² At sufficiently low coverage diffusion may become rate-limiting, but this

feature is omitted from the model. Recombinative desorption is assumed to occur between H atoms paired on surface dimers,^{2,6-8,12} so that

$$-\frac{d\Theta}{dt} = k \Theta_2 \quad (2)$$

Assuming that the preexponential factor for k is $2 \times 10^{15} \text{ sec}^{-1}$, as was found for H_2 desorption from Si(100) by Höfer *et al.*,¹² who took H-atom pairing into account in the analysis, the TPD peak temperature at high initial coverage implies an activation energy of 42 kcal/mol. The dependence of T_p on Θ_0 predicted by the model is shown in Fig. 2 for several assumed values of ΔH_{pair} . By comparing the experimental and model results, we infer ΔH_{pair} to be 5 ± 1 kcal/mol for H on Ge(100), which is only slightly less than the 6 ± 1 kcal/mol obtained^{8,12} for H on Si(100). The inferred value of ΔH_{pair} is quite insensitive to the assumed value of the preexponential factor. If the preexponential factor is assumed to be 10^{13} sec^{-1} , the activation energy must be reduced to 36 kcal/mol to be consistent with the value of T_p at $\Theta_0 = 1$. The values of T_p then predicted for $\Delta H_{\text{pair}} = 5$ kcal/mol are only slightly higher than those shown in Fig. 2 and are in equally good agreement with the data. At $\Theta_0 = 0.1$, for example, the predicted value of T_p increases by only 0.4 K by changing the preexponential factor, which is well within the error bars of ≈ 2 K associated with the uncertainty of ± 1 kcal/mol in ΔH_{pair} .

STM has not yet been applied to hydrogen adsorption on Ge(100), but infrared spectroscopic measurements¹⁶ provide independent evidence for at least a degree of preferential pairing of hydrogen. Infrared absorption features at 1979 and 1991 cm^{-1} for Ge(100) 2×1 :H at one-monolayer hydrogen coverage arise from the asymmetric and symmetric stretch modes of hydrogen atoms on doubly-occupied dimers and display distinct polarization properties.¹⁶ Distinct s- and p-polarized spectra, with a two-peak structure in the latter, were also observed for nominal exposures as low as 10 L,¹⁶ for which we estimate a hydrogen coverage of 0.3 ML. If occupation of the dangling bond sites were random, then only 30% of the hydrogen would have been present as doubly-occupied dimers and the spectrum would have been dominated by a one-peak structure.⁸ A degree of preferential pairing could occur during adsorption at a temperature where the adsorbed atoms are immobile by either a "hot precursor" mechanism²⁵ or by abstraction. If localization of adsorbing H atoms requires several bounces to dissipate the energy released by formation of the bond to the surface, adsorbing atoms will tend to settle preferentially into the deepest wells, viz., on already-singly-occupied dimers. Abstraction of surface hydrogen and halogen atoms by incident atomic hydrogen appears to be quite facile, at least on Si(100).^{1,26} If abstraction occurs even while adsorption is taking place at low coverage, abstraction of more weakly-adsorbed hydrogen (at singly-occupied dimers) will occur preferentially to that of more strongly-adsorbed hydrogen (at doubly-occupied dimers) due to a smaller activation barrier, which would also lead to an enhancement in the population of doubly-occupied dimers.

The similarity in the values of ΔH_{pair} for hydrogen on Ge(100) and on Si(100) is consistent with the similarity in π bond strengths in $\text{H}_2\text{Ge}=\text{GeH}_2$ and $\text{H}_2\text{Si}=\text{SiH}_2$ (≈ 25 kcal/mol).²⁷ The chemical similarity of germanium and silicon also extends to the geometric and electronic structure of their (100) surfaces. The basic structural units on reconstructed Ge(100) are buckled dimers,²⁸⁻³¹ with several ordered arrangements possible. The dimer bond length may be estimated as 2.41 Å from the measured³² value of its parallel component (2.34 Å) and the calculated³¹ buckling angle (14°).³³ This value is intermediate between the bond length in molecular digermenes, 2.21–2.35 Å,³⁴ and the single bond length of 2.44 Å in bulk germanium, and indicates a highly strained double bond. Similar considerations hold for Si(100), although the question of buckled versus symmetric dimers has been controversial. The preponderance of recent work³⁵⁻³⁹ indicates that the dimers are instantaneously predominantly buckled. The Si=Si dimer bond length, measured³⁵ as 2.32 ± 0.02 Å and calculated^{13,40,41} as 2.19–2.40 Å, is similarly indicative of a highly strained double bond. STM images of buckled dimers on Ge(100)²⁸ and Si(100)⁴² appear quite similar: the amplitudes of occupied and unoccupied states are greatest on the “up” and “down” atoms, respectively, of the dimer pair. The dimer tilt angle is significantly greater on Ge(100) ($\approx 14^\circ$) than on Si(100), measured³⁵ as 7° and calculated⁴⁰ as 7 – 10° . Both the larger tilt angle for germanium dimers and the apparently larger barrier to flipping^{28,31,40} are analogous to the deviation from and barrier to planarity in trans-bent $\text{H}_2\text{Ge}=\text{GeH}_2$ versus $\text{H}_2\text{Si}=\text{SiH}_2$.⁴³

What is the π bond strength in surface dimers on Ge(100) and Si(100)? Perhaps the cleanest definition for π bond strengths in molecules is the activation energy for rotation about the double bond,^{11,27} which is inapplicable to surface dimers. A second measure is based on the heat of hydrogenation of a double bond¹¹ and is equivalent to our definition of ΔH_{pair} .⁸ For $\text{H}_2\text{C}=\text{CH}_2$ and $\text{H}_2\text{Si}=\text{SiH}_2$ the two definitions of the π bond strength agree to within a few kcal/mol.¹¹ A less direct definition is the energy difference between the ground state singlet and the lowest-energy triplet configurations, which also agrees to within a few kcal/mol with the rotation barriers for $\text{H}_2\text{Si}=\text{SiH}_2$ and $\text{H}_2\text{Ge}=\text{GeH}_2$.^{11,27} However, the band structure of dangling bond surface states reflects the periodicity of the surface and provides no obvious measure of the π bond strength or of the propensity of H atoms to pair: bond formation is intrinsically a *local* process and chemisorption disrupts the surface periodicity and band structure. A simple localized- π -bond picture of the clean-surface electronic structure is contradicted by the dispersion of both the occupied (π or D_{up}) and unoccupied (π^* or D_{down}) bands in the Γ - \bar{J} direction (parallel to the dimer rows), with bandwidths of 0.8 and 0.7 eV on Si(100) 2×1 ^{36,39,44} and 1.0 and 0.35 eV on Ge(100) 2×1 ,^{29,30} respectively. The average band gap over the surface Brillouin zone is significantly *larger* for Ge(100), ≈ 1.9 eV,^{30,45} than for Si(100), ≈ 1 eV,^{39,46} showing the opposite trend to that of ΔH_{pair} and of molecular π bond strengths. Boland estimated the π bond strength in a slightly different way, as twice the difference in occupied-dangling-bond binding energies of unoccupied and singly-occupied dimers,⁷ the analogue of which gives a reasonable estimate of the π bond strength in $\text{H}_2\text{Si}=\text{SiH}_2$.⁴⁷ However, the dangling-bond electronic states probed by the STM are likely to be strongly

delocalized, as STM spectral measurements of the surface band gap yield similar results to those measured by conventional means^{30,39,46} on both Si(100)^{7,10} and Ge(100),²⁸ and are therefore of questionable applicability for determining a "local" π bond strength. While a delocalized interaction could in principle supply the driving force for pairing, a simple count of the singly- and doubly-occupied dimers in Boland's STM image of H on Si(100) after annealing to 630 K⁷ leads to an estimate of 6-7 kcal/mol for ΔH_{pair} using Eq. (1),⁴⁸ entirely consistent with the value inferred from the desorption kinetics^{8,12} but inconsistent with Boland's higher estimate⁷ for the π bond strength.

We conclude that the estimate of the π bond strength represented by ΔH_{pair} , 5 ± 1 kcal/mol for H atoms on Ge(100)2 \times 1 and 6 ± 1 kcal/mol for hydrogen on Si(100),^{9,13} quantitatively accounts for preferential pairing of hydrogen and that a reliable π bond strength cannot be readily extracted from the band structure of the clean surface. However, it would be intriguing to investigate the electronic structure of *isolated* un- and singly-occupied dimers, surrounded by doubly occupied dimers and prepared either by careful dosing of atomic hydrogen and/or by brief annealing of a hydrogen-saturated surface,⁷ to see whether a spectroscopic measure of the π bond strength could be obtained.

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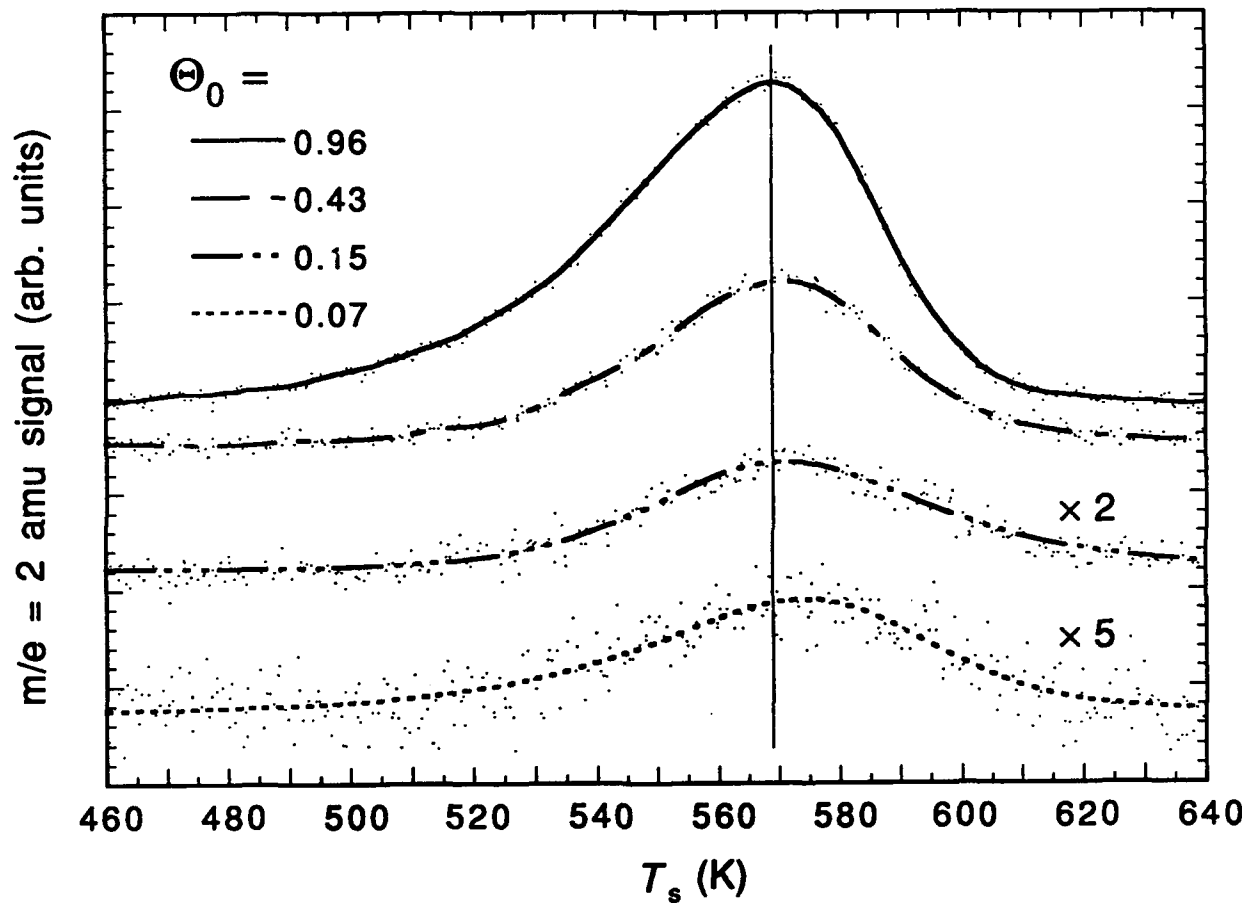


FIG. 1. Temperature-programmed desorption (TPD) data for H₂ following exposures to atomic hydrogen. The initial hydrogen coverage in monolayers, Θ_0 , is indicated for each trace. The vertical line indicates the TPD peak temperature for $\Theta_0 = 1$.

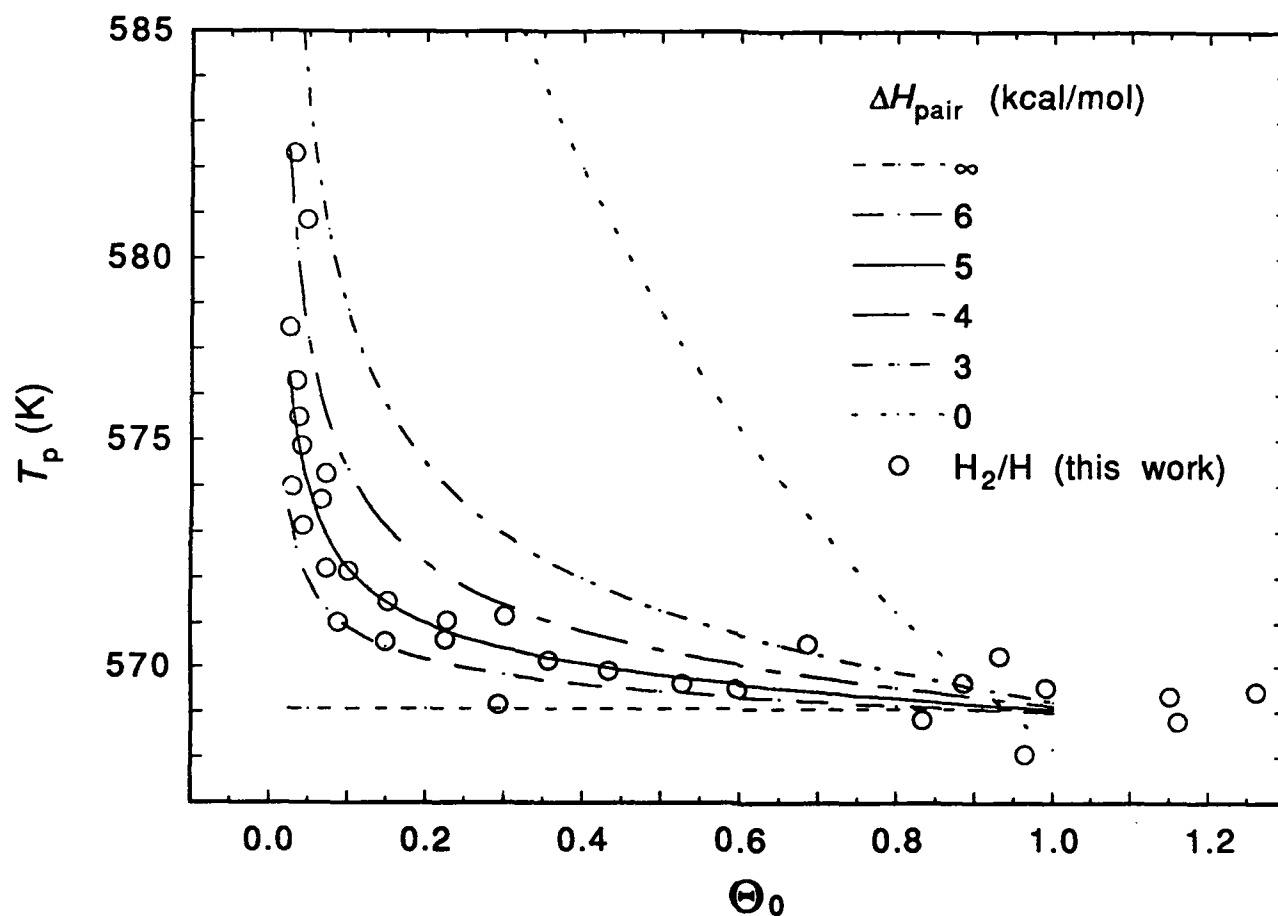


FIG. 2. Dependence of TPD peak temperature of H_2 on initial hydrogen coverage. Experimental results are shown together with predictions of the doubly-occupied dimer model as a parametric function of ΔH_{pair} . T_p was calculated using an activation energy of 42 kcal/mol and a preexponential factor of $2 \times 10^{15} \text{ s}^{-1}$ for k and a heating rate of 2 K s^{-1} .